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METHOD AND DEMONSTRATING INSTALLATION FOR RECOVERY OF TITANIUM AND TUNGSTEN OXIDES FROM SPENT SCR CATALYST
PART I – SCALING OF HYDRODINAMIC CAVITATION METHOD

Adrian CIOCĂNEA[1], Radu SAUCIUC[2], Ioan LEPĂDATU[2], Sanda BUDEA[1], Ștefan-Mihai ȘEFU[2], Ștefan-Mugur SIMIONESCU[1]

[1] University POLITEHNICA of Bucharest, adrian.ciocanea@upb.ro

[2] INOE 2000 – IHP Bucharest, sauciuc.ihp@fluidas.ro

Abstract: *Selective catalyst reduction (SCR) catalysts provided excellent results for the reduction of nitrogen oxide (NOx) emissions in diesel exhaust, due to a large range of operating temperatures, durability of deactivation and high conversion rate of NOx. Due to technological developments is unlikely to be replaced in automotive applications. As a result, the commercial efficiency of recovering critical materials is further sought in the context of reducing energy consumption and environmental impact. A hydrodynamic cavitation method is proposed in order to maximize the effect of destructuration of honeycomb monolithic support of SCR catalyst -* V_2O_5 *–* WO_3/TiO_2 *type - for extracting the crystalline titanium and tungsten oxides from the cordierite surface. High relative inlet pressure of 25 MPa is applied to a divergent nozzle for obtaining cavitation jets. In order to design the dedicated installation, the characteristics of the cavitation jets are analyzed: pressure drop in relation to the length and core diameter of the jet. The data are useful for settling down the optimum distance between the nozzle output and the target i.e. the honeycomb monolithic support of SCR catalyst. Best results are reported for 25 MPa where the ratio between jet core diameter and jet length is d/l=0.115. An inlet pressure at the nozzle input below 16MPa seems to be ineffective since no jet core is recorded.*

Keywords*: Selective catalyst reduction, diesel exhaust, hydrodynamic cavitation, submerged jet*

1. Introduction

Selective catalyst reduction (SCR) catalysts provided excellent results for the reduction of nitrogen oxide (NOx) emissions in diesel exhaust, due to a large range of operating temperatures, durability of deactivation and high conversion rate of NOx [1, 2]. Their advantages recommended them for integration in some diesel-powered light and heavy-duty vehicles [3-6]. SCR catalyst are composed primarily of anatase TiO_2 used as catalyst carrier, V_2O_5 as the active component and WO_3 acting as a promoter for thermal stability of the catalyst and offering resistance to sulfur contamination. The honeycomb - type monolithic support for the metal oxide species in the SCR catalyst is usually made of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$). The oxides of vanadium and tungsten contribute with about 40% at the total cost of the SCR catalyst [7]. The commercial V_2O_5 – WO_3/TiO_2 catalyst present a high tungsten (W) content, of about 7-10 wt% WO_3 by comparing with vanadium (V) content of only 0.5 – 1.5 % V_2O_5 [1, 8]. Chemical lifetime for the SCR is usually about 3 years and regeneration processes involving chemical and/or heat treatment is often considered in order to extend this lifetime, often doubling it. At the end of lifetime the deactivated SCR catalyst, after several regeneration cycles end up as waste and is disposed of in landfills. In order to avoid the soil contamination a strategy based on the recovery of valuable metals and regeneration of the rest of the spent catalyst must be considered [9]. In this paper a hydrodynamic cavitation method is scaled with the aim to include it in a demonstrator installation in order to maximize the effect of destructuration of honeycomb monolithic support of spent Selective Catalyst Reduction (SCR) catalyst - V2O5 – WO3/TiO2 type - for extracting the crystalline titanium and tungsten oxides from the cordierite surface.

2. Methods for recovering valuable metals from spent catalysts

The classical methods of recovering precious metals from car catalysts with ceramic base structure are of hydro-metallurgical type [10, 11] and of pyro-metallurgical type [10, 12]. From the point of view of the energy and environmental impact, each of the methods described raises specific problems: the hydro-metallurgical method involves wastewater treatment, while the pyro-metallurgical method involves high energy consumption and lower extraction rates.

Another class of methods refers to the mechanical ones: by friction and flotation or by ultrasonic cavitation. In the first method, the extraction is done in containers in which rotors with teeth are placed. They are calibrated such that between the rotors surface and the bottom of the vessel, an interstice of up to 0.3 ÷ 0.5 mm is formed [13, 14]. The grinding of the mixture, by means of the shear forces that appear between the particles, is carried out under conditions of flotation that facilitate a separation of the components.

The efficiency of the process is influenced by the residence time of the mixture in the container in the working range, the liquid/solid ratio and the size of the initial particles introduced into the device. The results reported in the literature [14] show that in fractions smaller than 300 µm the recovery percentage reached 81.2% for a residence time of approximately 60 min, the percentage being higher for the case where the introduced particles had larger dimensions – figure 1.

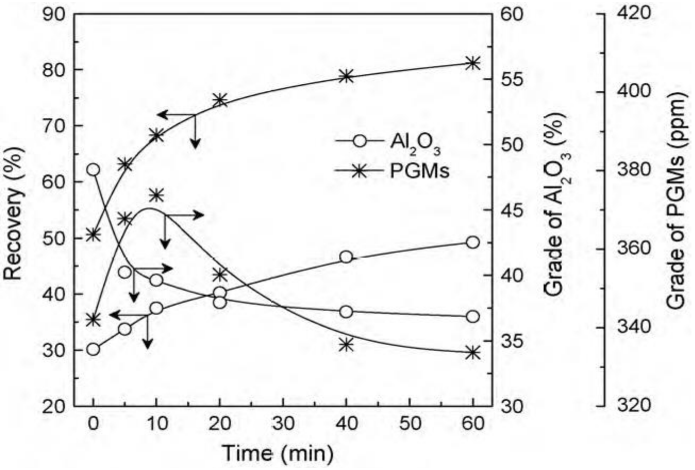


Fig. 1. The degree of recovery of Al_2O_3 and Platinic Metal Group (PMGs) for different time intervals (fractions below 300 μm) [14]

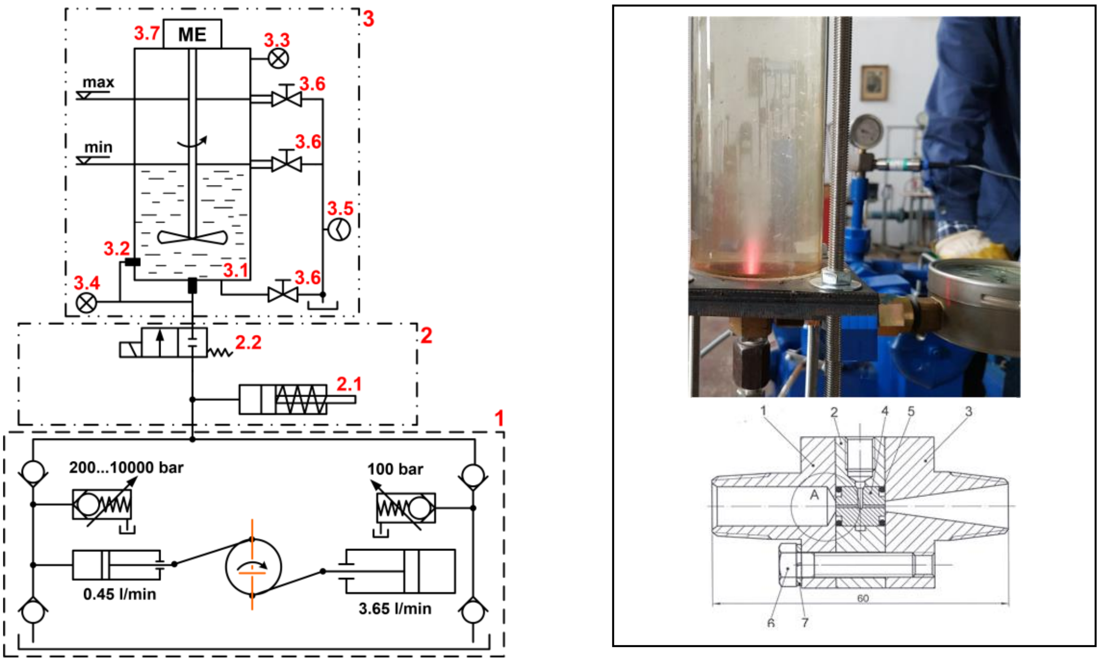
In the second method, the valuable metal extraction takes place by exposing the catalytic converter placed in an ultrasonic washing bath to the effects of (ultrasonic) cavitation [15]. The effects of cavitation are manifested by the detachment of catalytic material from the monolithic support that remains undamaged. Selective powders are obtained by adjusting a frequency in the range 10 ÷ 1000 kHz. There are no known studies in the literature to verify experimentally the above procedure.

A method that combines the two mechanical procedures described above is the hydrodynamic cavitation: (a) the mechanical effect of the cavitational jet produces high shear stresses between the particles of the mixture subjected to the procedure; (b) increasing the concentration of oxygen and free radicals in the biphasic liquid creates higher premises of oxidation reactions with metals.

Hydrodynamic cavitation, respectively the creation of cavitational jets, can be achieved by at least two methods: (a) by using an intermediate fluid (ex. N_2) [16] or (b) by using a high-pressure volumetric pump [17]. By increasing the inlet pressure in a nozzle, the cavitation phenomenon becomes more active. For different working pressures and shapes of the nozzle, the jet is characterized by the appearance of vapors and/or air bubbles, i.e. by the manifestation of cavitation with vapor bubbles and air bubbles. The two types of cavitation appear simultaneously if the liquid is not degassed. It is known that only the bubble cavitation has an erosion effect [18] and therefore it is desirable that the shape of the nozzle, the ratio of upstream/downstream pressures and the degree of oxygenation of the liquid ensure its occurrence. The existence of the gas bubble cavitation has a mechanical role, since the bubble cloud is destroyed only at the impact with a solid boundary or at a distance if there is enough space available for the pressure to play this role. Experimental studies have revealed the connection between the liquid and nozzle parameters and the two types of cavitation [17].

3. Experimental set-up

The experimental stand was built using a pressure source i.e a volumetric piston pump that provided a maximum pressure of 25 MPa. The pump was mounted to a device with a divergent nozzle with a minimum diameter of 0.5 mm. The working pressure was monitored in real time by means of a digital pressure gauge connected through a data acquisition board to a computer. It was thus possible to determine the number of cavitation cycles that the pump induced in the work room. In figure 2 (a, b, c) the elements of the experimental stand and of the divergent nozzle are presented.



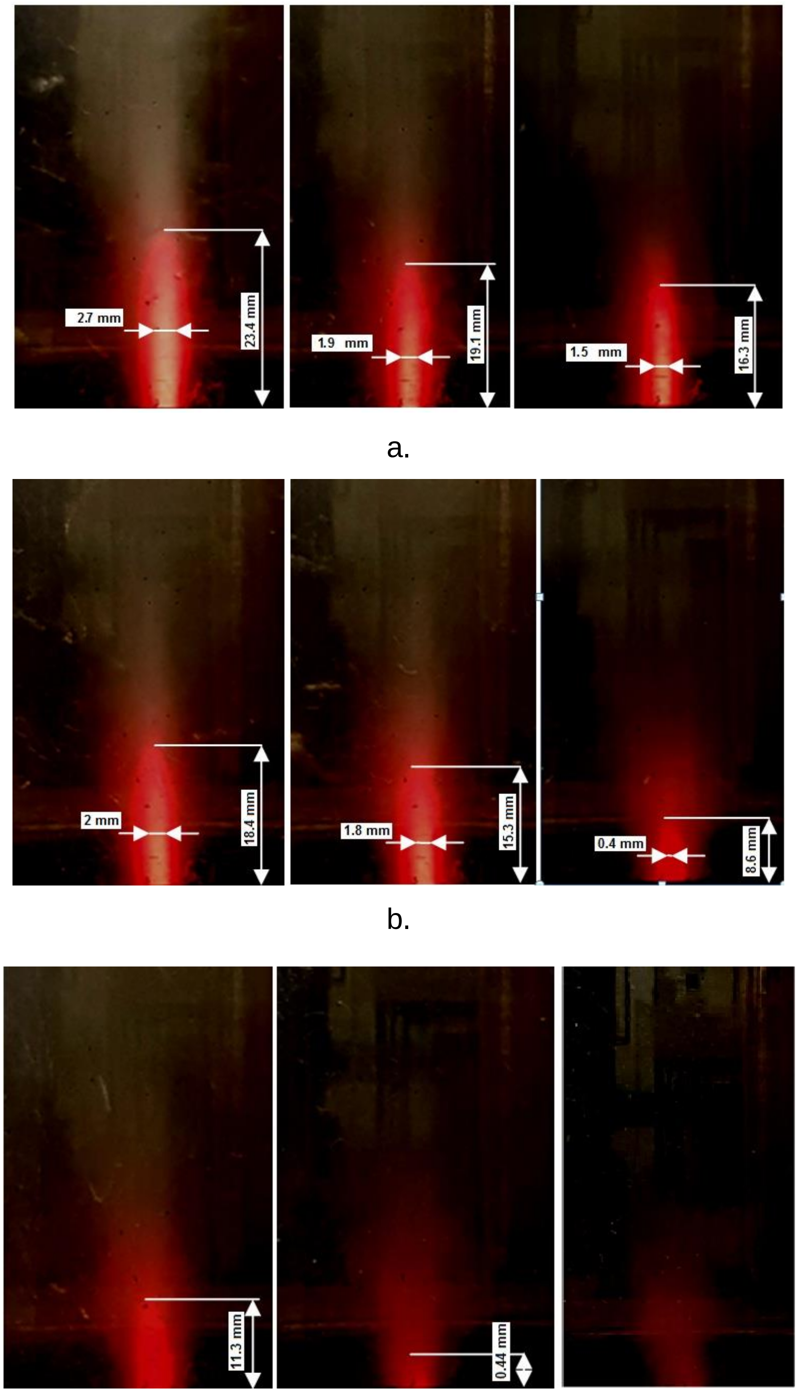
a. b. c.

Fig. 2. Experimental set-up: (a) Cavitation jet system (1. Plunger pump system; 2. Pressure distribution system: 2.1. Accumulator, 2.1. Electric distributer; 3. Test chamber: 3.1., 3.2. Nozzle, 3.3. Low pressure transducer, 3.4. High pressure transducer, 3.5. Flow indicator, 3.6. Valves, 3.7. D.C. motor and propeller) and (b, c) Cavitation nozzle (transparent cylinder, nozzle $\phi = 0.5$ mm)

The pressure drop in the nozzle was measured by using a digital pressure gauge (3.4), as well as the downstream pressure (3.3). The cavitational jet was highlighted with the help of a red-light planar laser that allowed the determination of the jet dimensions.

4. Results

The plunger pump was used in order to deliver three fixed upstream pressures in the nozzle: 250, 160 and 80 MPa. The pressure drop in the divergent nozzle was measured for each inlet pressure at downstream pressure values of 0.0, 0.05 and 0.1 MPa respectively. For each case, the geometry of the cavitational jet was assessed by analyzing a group of photos obtained with a frequency of 1/300 s. The results are presented in figure 3 (a, b, c), where the core diameter and length of the cavitational jet are related with the pressure drop in the nozzle.



a.

b.

c.

Fig. 3. The geometry of the cavitational jet
a) upstream pressure – 25 MPa and downstream pressure 0.0 MPa, 0.05 MPa and 0.1 MPa;
b) – 16 MPa and downstream pressure 0.0 MPa, 0.05 MPa and 0.1 MPa;
c) – 8 MPa and downstream pressure 0.0 MPa, 0.05 MPa and 0.1 MPa;

Table 1 presents the pressure drop in the nozzle and the *d/l* ratio, where *d* is the jet core diameter and *l* is the jet length.

Table 1: Pressure drop in the nozzle and *d/l* ratio

Upstream Pressure MPa	Downstream pressure MPa	Pressure drop MPa	*d* mm	*l* mm	*d/l* -
25	0.00	0.85	2.7	23.4	0.115
25	0.05	0.72	1.9	19.1	0.099
25	0.10	0.56	1.5	16.3	0.092
160	0.00	0.75	2.0	18.4	0.110
160	0.05	0.30	1.8	15.3	0.110
160	0.10	0.16	0.4	8.6	0.046
80	0.00	0.63	-	11.3	-
80	0.05	0.16	-	4.4	-
80	0.10	0.00	-	-	-

The best results are reported for the case where the value for upstream pressure is 25 MPa with no downstream pressure and the ratio has the highest value, *d/l* = 0.115. The maximum length of the cavitational jet is 23.4 mm. For the upstream pressure of 16 MPa the ratio *d/l* = 0.110 – close to the best result reported – but the length of the cavitation jet is shorter, *l* = 18.4 mm. Therefore, when designing the demonstrator installation, the optimum distance from the nozzle outlet to the honeycomb monolithic support of SCR catalyst as target should be in the range of 18÷20 mm in order to maximize the cavitation effect.

5. Conclusions

A hydrodynamic cavitation method is proposed in order to maximize the effect of destructuration of honeycomb monolithic support of SCR catalyst. An upstream pressure of 25 MPa is applied to a divergent nozzle for obtaining cavitation jets and various downstream pressures were settled down in order to assess the impact on jet geometry. The best results of the study will be used for optimizing a dedicated installation i.e. settling down the distance between the nozzle outlet and the honeycomb target. The characteristics of the cavitation jets are analyzed: pressure drop in relation to the length and core diameter of the jet. Best results are reported for 25 MPa where the ratio between jet core diameter and jet length is *d/l*=0.115. An inlet pressure at the nozzle input below 16 MPa seem to be ineffective since no jet core is recorded.

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